



Application Number : 09/898,823

Applicants : Chris Eberspacher and Karen L. Pauls

Title : "Method for Forming Particulate Materials"

Examiner : Elena Tsoy / 1762

Declaration Related to US Patent No 5,928,405

The inventors of the above mentioned application swear that they built and tested the invention disclosed in Application No 09/898,823 before the May 21, 1997 filing date of US Patent No 5,928,405. Attached as documentation are portions of a report to the US Department of Energy written by the inventors.

Chris Eberspacher

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Date Sept 12, 2003

Karen L. Pauls

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Date 9/12/03

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U.S. Department of Energy
SMALL BUSINESS INNOVATION RESEARCH
SOLICITATION NO. DOE/ER-0653
PHASE II APPLICATION COVER SHEET

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Phase I Application No. 41108-96-I DOE Grant No. DE-FG03-96ER82300

Project Title: Improved Processes For Forming CIS Films

Topic No. 24 Subtopic b Topic Title _____

Submitted by: (Firm Name) UNISUN

Amount Requested (Phase II) \$ 750,000 Proposed Duration: 24
(Not to exceed \$750,000) (Months)

CERTIFICATIONS AND QUESTIONS

1. The above organization certifies that it is a small business and meets the definition stated in Section 2.3 of solicitation No. DOE/ER-0653. Yes X No _____
2. A minimum of one-half of the funded research or analytical effort will be performed by the applicant organization. Yes X No _____
3. Is the small business delinquent on any Federal debt? (If "Yes," please attach an explanation.) Yes _____ No X
4. If the proposed project does not result in an award, does the applicant permit the government to disclose the technical abstract of the application, and the name, address, and telephone number of the business official to any inquiring parties? Yes X No _____

ENDORSEMENTS

Principal Investigator (See Section 1.5 of Solicitation No. DOE/ER-0653.)

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Signature of Principal Investigator Date

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Proprietary Notice (If Applicable, See Section 5.4 of Solicitation No. DOE/ER-0653)

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Phase I focused on four key tasks:

- a. demonstrate the production of fine-grain precursor particles
- b. demonstrate the deposition of precursor films on substrates
- c. demonstrate the conversion of precursor films to device-quality CIS layers
- d. calculate a projected cost of CIS films formed using these techniques

All of these tasks were fully completed. A summary of the key results follows.

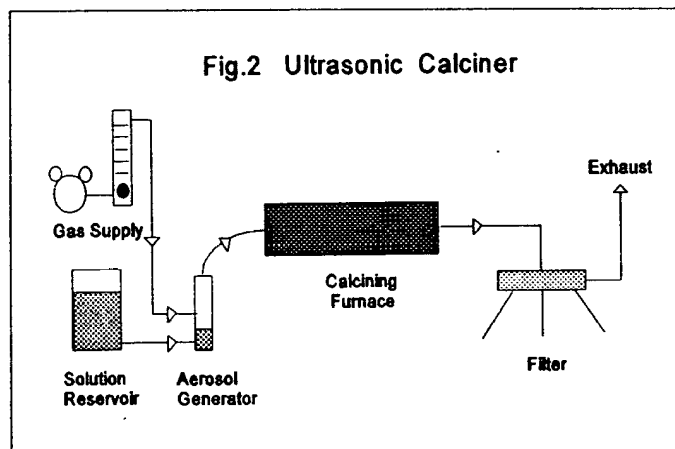
4.1 Demonstration of the production of fine-grain precursor particles

This task was aimed at demonstrating that fine-grain particulate precursors could be produced with the desired properties.

The process used to produce particulate precursor materials is calcination of atomized reactant solutions. Aqueous solutions are prepared using metal salts, e.g. nitrates of copper, indium and gallium. Reactant solutions are atomized into a fine aerosol using an ultrasonic transducer. The aerosol is transported into the calciner by carrier / reactant gases, such as oxygen, nitrogen and nitrogen/hydrogen mixtures. The calciner itself is a quartz tube furnace with specially-designed end-caps and exit plumbing. Aerosol droplets and reactant gases react in the calcining furnace to form precursor particles. Particles are collected on a polymer filter membrane. The basic equipment set is sketched in Figure 2.

The key materials properties of precursor particulates are particle size, shape, density and composition. The key characteristics of the particle production process are materials use efficiency (i.e. the efficiency with which reactant source materials are converted into and collected as usable precursor particles), ease of process control, and process productivity.

The mean size of precursor particles produced in this manner is a function of droplet size, solution concentration, droplet and particle interactions, and particle composition. Assuming spherical dense particles, neglecting droplet and particle interactions, and assuming complete reactant



reaction one calculates:

$$[\text{Eq. 1}] \quad \text{particle dia.} = [\text{solution molarity} \times \text{mole mass} / \text{particle density}]^{1/3} \times \text{droplet dia.}$$

UNISUN's ultrasonic aerosol generator operates at ca. 1.5 MHz and produces 4 - 5 μm diameter droplets. At this droplet diameter, solid spherical $\text{CuInO}_{2.5}$ particles of ca. 6.8 g/cm^3 average weight density and ca. 100 nm average diameter requires, for example, a reactant solution (e.g. of copper and indium nitrates dissolved in water) concentration of ca. 0.25 mM (i.e. 0.25 mM each of Cu and In). One can similarly calculate the reactant solution concentrations needed to make solid particles of various diameters of different materials (e.g. CuIn_xO_y , $\text{CuIn}_x\text{Ga}_y\text{O}_z$, CuO_x , Cu, Cu_xIn_y , etc.).

Table 1 summarizes the results of a subset of the calciner runs made in Phase I. Three key accomplishments are immediately evident. First, the ultrasonic calcination process can yield particles in the desired size range (i.e. 100 - 250 nm). The distribution of particle diameters was not quantified, but the distribution appears reasonably narrow (e.g. few very small or very large particles are evident). Second, the process can yield fine-grain precursor materials of a variety of binary and multinary compositions, including oxides and metals. Third, the droplet-to-particle reaction follows the simple relation in Equation 1 above, indicating that the assumptions about droplet and particle interactions, particle density, and reaction completion are valid.

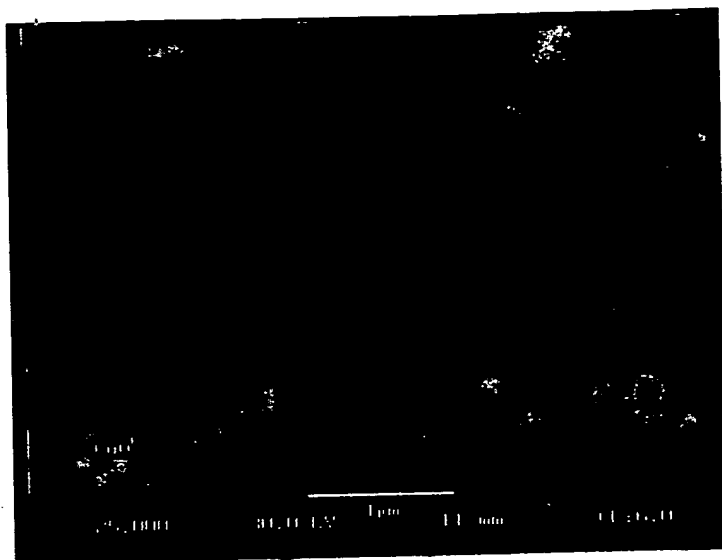
Table 1. Precursor Particle Size

Precursor Material	Solution Molarity (mole/L)	Target Particle Size (microns)	Actual Particle Size (microns)
Cu / In_2O_3	0.39×10^{-3}	0.10	0.10 - 0.15
CuO	19.7×10^{-3}	0.30	0.25 - 0.50
$\text{CuInO}_{2.5}$	0.50×10^{-3}	0.25	0.10 - 0.25
$\text{CuInO}_{2.5}$	0.24×10^{-3}	0.10	< 0.10 - 0.20
$\text{Cu}_2\text{O} / \text{In}_2\text{O}_3$	0.24×10^{-3}	0.10	< 0.10 - 0.20
$\text{CuIn}_{.75}\text{Ga}_{.25}\text{O}_{2.5}$	0.25×10^{-3}	0.10	0.10 - 0.15

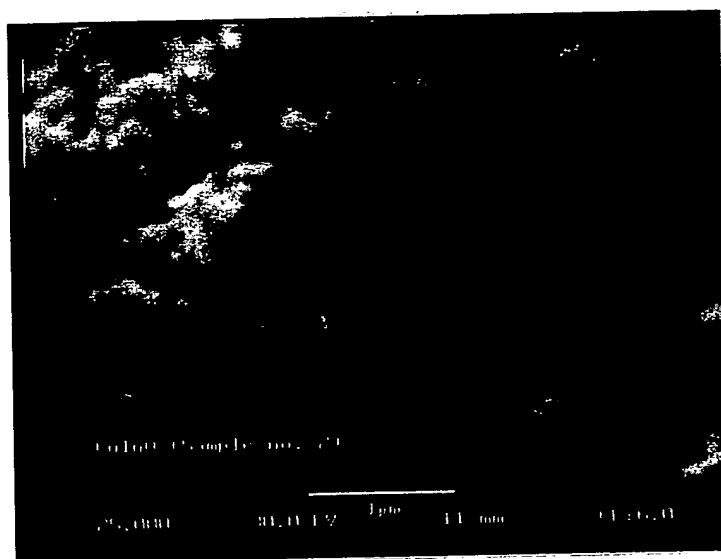
Scanning electron microscopy (SEM) images show that the precursor particles are spherical, properly sized, and non-agglomerated (Fig. 3 a, b & c). The spherical, dense nature of the precursor particles is desirable to obtain dense, cohesive precursor layers

Figure 3

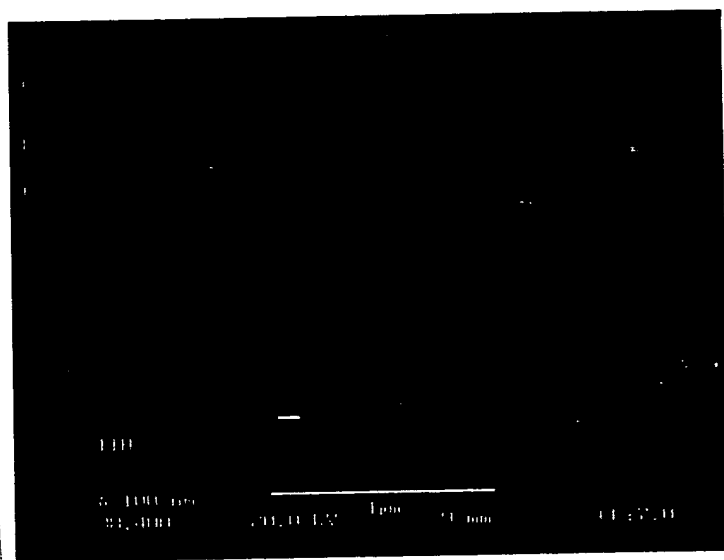
a. $0.3\ \mu\text{m}\ \text{CuO}$



b. $0.25\ \mu\text{m}\ \text{CuInO}_{2.5}$



c. $0.1\ \mu\text{m}\ \text{CuInO}_{2.5}$



that yield hollow spheres and other less desirable particle properties. UNISUN's ultrasonic calcination process circumvents these problems for these materials provided one is attentive to reaction temperature profiles, reaction rates and calciner residence times.

Table 2 summarizes the results of another subset of the calciner runs made in Phase I. Three key accomplishments are immediately evident. First, 40 - 60% of the reactants prepared as solutions are subsequently captured as usable particles. This is a good materials use efficiency given the low-volume production rate and research-scale equipment set of Phase I. Consultations with Rocketdyne and with Nanochem Inc. in Albuquerque, NM indicates that aerosol calcination processes can be scaled to high-volume production and that materials use efficiencies can be quite high in larger-volume production. Second, precursor composition can be easily controlled over the full range of interest (e.g. Cu/In atomic composition ratio = 0.6 - 1.2) by varying the relative concentrations of reactants in the reactant solutions. Alloying components (e.g. Ga to make CIGS) and advantageous low-level additions (e.g. Na to facilitate CIS film crystalline properties) can be added by simply adding the appropriate soluble reactant (e.g. gallium nitrate, sodium nitrate, etc.). Similarly, the chemical pathways developed for spray pyrolysis deposition of CuInSe_2 could be used in the ultrasonic calcination process to form nanopowder chalcogenides. Third, the measured Cu/In ratio is roughly equal in the reactant solutions and the precursor powders, indicating that - unlike other CIS formation processes - losses of indium (i.e. the most expensive of the three primary constituents in CIS) are minimal. This bodes well for the overall cost effectiveness of the process.

Table 2 and Figure 4 indicate that precursor characteristics (e.g. composition and structure, ergo color) are a function of reaction gas. Calcination in pure oxygen and pure nitrogen both yield oxides, but the powder compositions are considerably different in ways that can facilitate precursor film deposition and conversion to chalcogenide films. X-ray diffraction (XRD) data indicates that calcination of nitrates in oxygen yields single-phase oxides or mixtures of ternary oxides and indium oxide, e.g. single-phase $\text{CuIn}_x\text{Ga}_y\text{O}_{2.5}$ or $\text{CuInO}_{2.5} + \text{In}_2\text{O}_3$ (Fig. 5a, b). Calcination of nitrates in nitrogen yields binary oxides, e.g. $\text{Cu}_2\text{O} + \text{In}_2\text{O}_3$, not $\text{CuInO}_{2.5}$ (Fig. 6). Calcination in a strongly-reducing environment (e.g. N_2/H_2 mixtures) yields unoxidized metal powders (e.g. Cu) and/or mixtures of metals and metal oxides (e.g. $\text{Cu} + \text{In}_2\text{O}_3$) (Fig. 7). It's of particular interest that Cu metal and Cu metal / In oxide precursor particles can be prepared using UNISUN's techniques. Commercial nanoparticle processes (e.g. vapor-phase reactions in vacuum) are generally limited to oxide materials or to noble metals that do not readily oxidize. UNISUN's ultrasonic calcination process yields $\text{CuInO}_{2.5}$, CuO_x , $\text{Cu}_2\text{O} + \text{In}_2\text{O}_3$, Cu, and stable $\text{Cu} + \text{In}_2\text{O}_3$ precursors. The ability to form a full range of oxide and metallic precursors considerably broadens the precursor-layer-to-absorber-film conversion process options.

The success of the ultrasonic calciner method for forming particulate precursors obviated the need to test the various "fall-back" precursor formation options identified in the Phase I proposal.

Table 2. Precursor Composition Data

Run ID	Type of Material	Particle size	Percent powder collected	Meas. Cu/In sol'n	Cu/In powder EDAX	Cu/In powder ICP	Gas	Color
C6	CuO	0.3		NA	NA		O ₂	black
C7	CuO	0.3		NA	NA		O ₂	black
C8	CuInO _{2.5}	0.25			1.11		O ₂	green
C10	CuInO _{2.5}	0.1			1.06		O ₂	green
C11	CuInO _{2.5}	0.1	30				O ₂	green
C14	Cu / In ₂ O ₃	0.25	60		0.65		7%H ₂ /N ₂	blue-black
C15	Cu	0.25	37	NA	NA		7%H ₂ /N ₂	copper
C16	CuInO _{2.5}	0.1	53		0.74		O ₂	green
C17	CuInO _{2.5}	0.1	59		0.76	0.71	O ₂	green
C18	Cu ₂ O / In ₂ O ₃	0.1	51				N ₂	yellow
C19	Cu ₂ O / In ₂ O ₃	0.1	39		0.67		N ₂	yellow
C20	CuInO _{2.5}	0.1	40				O ₂	green
C21	Cu ₂ O / In ₂ O ₃	0.1	44	0.8			N ₂	yellow
C22	CuIn ₇₅ Ga ₂₅ O _{2.5}	0.1	47		0.96	0.9*	O ₂	green
C23	Cu / In ₂ O ₃	0.1	63	1.07	1.12	1.07	10%H ₂ /N ₂	blue-black
C24	Cu ₂ O / In ₂ O ₃	0.1	38		1.05		N ₂	yellow
C25	Cu ₂ O / In ₂ O ₃	0.1	35		1.23		N ₂	yellow

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